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Thermochromic and photochromic behaviour of “chameleon” diamonds

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Abstract

Chameleon diamonds typically change color from greyish-green to yellow when they are heated or cooled (thermochromic behaviour) or kept in the dark (photochromic behaviour). Those diamonds are type Ia with A aggregates largely dominating the nitrogen speciation. They contain moderate to high amounts of hydrogen, in addition to some isolated nitrogen and traces of nickel. Their UV Visible spectrum comprises the continuum typical of type Ib material, the 480 nm band and a broad band centred around 800 nm. It is mainly modified in the red part of the visible spectrum when the color change occurs. We here propose an electronic model consistent with all observed color behaviours, based on the premise that yellow is the stable color whereas green is the metastable one. The chameleon effect is possibly linked to a nitrogen–hydrogen complex.

Keywords: Natural diamond; Chameleon effect; Hydrogen; Optical properties

1. Introduction

Chamelelon diamonds are an unusual variety of colored diamonds. They exhibit a noticeable color change when they are heated to about 200 °C and also when they are kept in the dark for an extended period of time. Hence, they are both thermochromic and photochromic. Their color generally changes from greyish yellowish green to brownish- or orangey-yellow. First considered as extreme rarities among gemmologists, they are now a little more common in the trade, perhaps due to increased interest in diamonds of all colors, including desaturated tones that were before considered unattractive. Although no production statistics are available for this particular category, it is also possible that more hydrogen-rich diamonds – and therefore arguably more chameleon diamonds – are produced currently (for instance in the Argyle Mine in Australia or the Jwaneng Mine in Botswana) than in the past. This article summarizes our observations on more than forty such colored diamonds. It includes observations on the 22-ct Green Chameleon diamond and a 31.31 ct oval gem, the largest documented chameleon diamonds to date. It is important to note that, to the best of our knowledge, no chameleon diamond issuing from synthesis or treatment has been documented. Using the identifying characteristics of chameleon diamond that we have studied, we propose a definition of chameleon diamonds, in order to avoid ambiguities with other colored diamonds presenting some kind of change of color. Finally, we also propose for the first time a possible mechanism responsible for the color change.

2. Background information

Chameleon diamonds are mentioned in the gemmological literature, but past reports contain only limited information on them. The earliest mention we know of such diamonds is in the 1866 novel by French writer Jules Verne “The Star of the South”: “This [ ] is one more curiosity, which puts this stone in the rare family of “chameleon diamonds” [ ] it is usually to an abrupt variation in temperature that these colour changes in coloured diamonds are due, and they have been mentioned fairly often to scientific societies”. The GIA Diamond Dictionary [1] indicates that the first of these diamonds was recognized and described in 1953. On several occasions since then, they have been briefly mentioned by gemmologists (see, e.g., Crowningshield [2]; Fryer et al., [3], Koivula and Kammerling [4] and Emms [5]). We

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believe that the 1982 citation from GIA's "Gem Trade Lab Notes" column is the first published photographic record of the color change observed in chameleon diamonds. In these past reports, these chameleon diamonds are generally described as having a greyish-green color (with some yellow or brown component) at room temperature under normal lighting conditions, and then becoming yellow to orange-yellow when kept in the dark or when the temperature is increased (typically placing the stone above the flame of an alcohol lamp). This thermochromic behaviour was previously taken as the definition of chameleon diamonds [6]. In either case, the color change is reversible, and the diamond reverts back to its original yellowish- or greyish-green when it is exposed to light or as it cools, generally within a few minutes or less. A detailed study of a collection of 39 chameleon diamonds was recently published by Hainschwang et al. [7]. They described a "classic" chameleon group with the photochromic and a thermochromic behaviour described above, and a "reverse" group, diamonds which are yellow and become green by heating only.

In infrared spectroscopy, chameleon diamonds are almost pure type IaA with very high nitrogen concentrations. They also contain typically unusually large amounts of hydrogen which led to these diamonds being classified as "H-rich" [6]. The presence of a band near 1240 cm^{-1} has been observed so far only in stones with a Ib character [8,9], including some chameleon diamonds [10]. This is suggestive that chameleon diamonds may have a minor Ib character, even if there is no comment as to the presence or absence of the 1344 cm^{-1} band, considered positive proof of Ib character.

Fritsch and colleagues [6,11] published a room-temperature spectrum of a typical chameleon diamond which presents a broad 480 nm band, a moderate peak at 425 nm and a 415 nm band (N3 centre) superimposed upon an absorption continuum which increases toward the ultraviolet. They also noted a weak and broad band centred around 700 nm. This refines previous results by Scarratt [12]. Hydrogen-related features (563 and 474 nm) were also detected in UV Visible spectra of some chameleon diamonds [7] but are absent in some others (e.g. 31.31 ct).

Photoluminescence spectra revealed the presence of the 701, 794, 882 nm bands which are interpreted as being linked to a nickel-related centre in chameleon diamonds [7]. Small concentrations of nickel were also revealed by EDXRF [7,10].

Chameleon diamonds present a typical strong yellow ultraviolet fluorescence in both SW and LW, and a strong and long lasting phosphorescence [5–7,13]. Detailed examinations [14] showed that in chameleon diamonds this luminescence is generally uneven. Indeed some short-wave UV topographic observations have shown that chameleon diamonds present a mixed growth history, qualified by De Weerdt and Van Royen as "unusual" [10]. In some samples, Chabert and Reinitz [15] also noted a blue to violet luminescence when some unusual chameleon diamonds were placed on an intense visible light.

Unfortunately, the term "chameleon" has also been applied rather loosely to other diamonds which change color under different conditions. Gill [16] describes as the first "chameleon diamond" a historical diamond that changed from "rose red" to brown when moved from the dark into the sunlight. He also refers to three "chameleon diamonds", brownish yellow by incandescent light and greener in sunlight. Raal [17] briefly mentions some naturally- and laboratory-irradiated green diamonds that become yellow upon heating at 400 °C in the dark, and reverted to their greener, stable color upon exposure to light. He refers to this as "chameleon behaviour". We believe that these situations represent a different color phenomenon than what we are describing, and they are not discussed further here.

Finally, Van Bockstael [18,19] identified three different "types of color changes" in some diamonds, the first described is the "classic" chameleon effect whereas the second one, which occurs mostly in pink diamond from Argyle (Australia), is a change from pink to brownish pink and the third, observed in only one stone, is a change from faint pink to colorless. The last two color changes occur after exposure to UV radiation and so cannot be considered as chameleon behaviour according to most authors' definition.

3. Materials

We studied about 45 faceted chameleon diamonds, ranging in weight from 0.013 to 31.31 ct. They were obtained on loan from private parties. This sampling is representative of chameleon diamonds found on the market today. Part of this study was the 31.31 ct, the largest of our study group, and the 22-ct Green Chameleon Diamond, both already documented in the past: [15,20] and [14,21] respectively.

The country of origin of most stones is unknown, including the 31.31 ct. However, one diamond came from the Argyle mine in Australia, and the 22.28 ct Green Chameleon Diamond was found in the Lorenzo Marquez area of Angola. Roskin [22] describes an appreciable amount of chameleon diamonds from a mine in China, some of the diamonds studied here might come from this country.

4. Methods

Ultraviolet luminescence was examined under darkroom conditions, using a GEM instruments unit (4 W) with both long wave (365 nm) and short-wave (254 nm) ultraviolet radiation, with the sample placed against a non-fluorescent black background. As UV lamps typically emit a small amount of visible light in the violet and blue range, which may induce violet to blue reflections on the objects illuminated, attention was paid to avoid interpreting these reflections as emissions. A gemmological microscope was used with a variety of illumination techniques, including darkfield, transmitted light, polarized light and oblique illumination.

The ultraviolet visible absorption spectra were obtained using a Varian Cary 5G recording the spectrum in the range 300 to 850 nm, at a resolution of 1 or 0.5 nm. A cryogenic cell was adapted to record spectra at both room and liquid nitrogen temperature.

Visible–near-infrared absorption spectra in the 400–1000 nm range at high temperature were obtained with a portable home-made system, equipped with an Ocean Optics SD2000 dual channel spectrometer with a resolution of 1.5 nm. A 2048-

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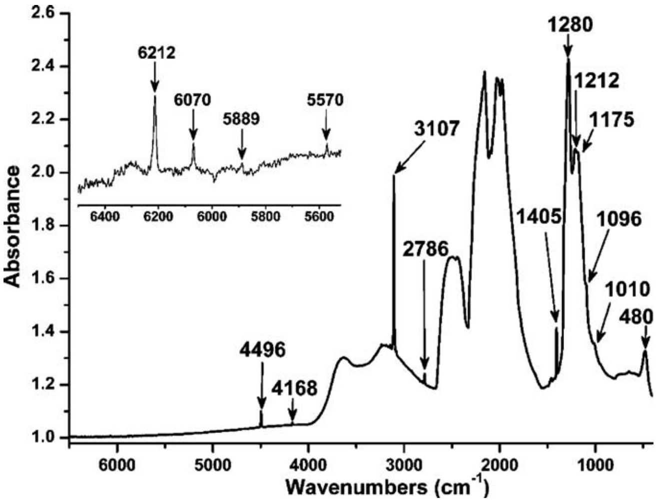

Fig. 1. Typical infrared spectrum of an H-rich chameleon diamond. Inset: range 5500–6500 cm^{-1} (see text for peak interpretation).

element linear silicon CCD detector was employed, samples were analyzed in an integrating sphere.

The infrared absorption spectra were obtained using a Bruker Vertex 70 (DLaTGS detector) with a beam condenser (the beam height changes from 7 mm to approximately 0.5 mm), and at 2 cm^{-1} resolution.

Some luminescence spectra were recorded with a Jobin-Yvon Fluorolog-3 at a resolution of 1 nm with an air-cooled xenon lamp as excitation source, others with a portable system using a 532 nm semiconductor laser, with the same Ocean Optics SD2000 spectrometer and CCD detector as described above, at a resolution of 1.5 nm. Diamonds were cooled at 77 K with liquid nitrogen for the Vis/NIR and PL spectra for a 365 nm excitation wavelength.

5. Gemmological properties

5.1. Color, thermochromic and photochromic behaviour

At room temperature, most chameleon diamonds have a fancy greyish-green to green-yellow color. However the range of the color of chameleon diamonds extends from fancy dark green to fancy greenish grey to fancy brownish or greyish yellow. All these colors have in common a low saturation and generally a medium lightness even if some atypical samples are very light or dark.

When heated, the color of chameleon diamonds changes generally to yellow, between 125 and 135 °C, depending on the size of the diamond. The thermochromic colors grade typically from fancy brownish yellow to fancy intense yellow although they could reach fancy orange-yellow to fancy intense orangey-yellow for exceptional samples.

This color change generally takes 30 s to 1 min. Once the source of heat is removed, the stone returns to its previous color in 1 to 3 min.

For all chameleon diamonds we checked for photochromic behaviour we did find such behaviour. For most stones, this can be easily observed by leaving the gem in a light-tight container such as a safe overnight. When opening the safe in the morning, the stones are considerably yellower than when the safe was closed. However, for the two large chameleon diamonds (the 31.31 ct and the 22-ct Green Chameleon) both had to be kept in the dark for a week to a month (this was variable from one experiment to the next) before they appeared yellow on opening the dark box in which they were stored.

Because no process can help holding the diamond in its color after light is shone on it, it is impossible to objectively grade this particular photochromic color by contrast to the thermochromic color. However, careful observations indicate that this color is in general a less saturated yellow than the color seen during heating. For example, one stone was greyish yellow coming out of darkness, but orange-yellow when heated. After being exposed to standard lighting conditions, chameleon diamonds revert to their color in approximately 1 min.

6. Microscopy

6.1. Color distribution

The majority of chameleon diamonds show an homogeneous color. However, in 13 of our samples we could observe an inhomogeneous color distribution, generally in the form of banding or sectorial zoning. The contrast is generally between a near colorless to yellow color in the apparently octahedral sectors and a more desaturated greyish-green color in likely cuboid sectors.

6.2. Spectroscopy

The main purpose of this study is to establish the common denominator among chameleon diamonds. In the discussion all the defining characteristics will be brought together to propose a definition and a possible mechanism for the color change.

6.3. Infrared absorption

The mid-infrared spectrum of chameleon diamonds is typical of a nearly pure type IaA to type IaA/B with [A]≫[B] diamond (Fig. 1). Absorptions at 1280 cm^{-1}, 1212 cm^{-1} and 480 cm^{-1} are related to A aggregates whereas those at 1175 cm^{-1}, 1096 and 1010 cm^{-1} are related to B-aggregates.

Table 1
Infrared hydrogen-related peaks

Peak value (cm^{-1})	Peak interpretation
1405	$\nu_{bending}$ of the C–H bond
2786	$2\nu_{bending}$ of the C–H bond
3107	$\nu_{stretching}$ of the C–H bond
3236	Related to the N–H bond [9]
3098	Related to the ^{13}C–H [9,23]
4168	$3\nu_{bending}$ of the C–H bond
4496	$\nu_{bending}+\nu_{stretching}$ of the C–H bond
5570	Possibly $4\nu_{bending}$ of the C–H bond
5889	$2\nu_{bending}+\nu_{stretching}$ of the C–H bond
6070	$2\nu_{stretching}$ of the C–H bond

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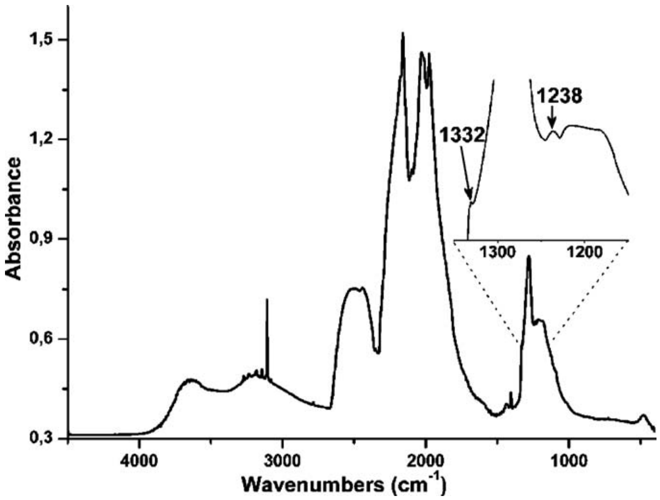

Fig. 2.

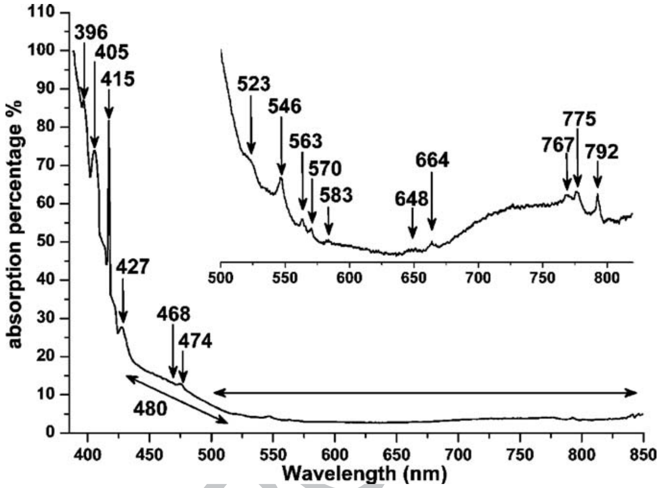

Fig. 4.

In addition, there are several sharp bands in the mid- and near-infrared spectra that have been attributed to the presence of hydrogen as an impurity [11] inducing vibrations of a C–H bond (see Table 1). Concentration of hydrogen varies in our samples from a medium to a high quantity, that is the 3107 cm^{-1} peak height varies from about half the peak height of the intrinsic two-phonon band at 2450 cm^{-1}, to about double the height of that intrinsic peak.

Regarding the partial type Ib character of chameleon diamond, only a weak shoulder at 1130 cm^{-1} is at best visible, but no 1344 cm^{-1}, whereas many peaks indirectly related to isolated nitrogen [9] are visible. Those ones are weak to very weak but distinct: 1238 (Fig. 2), 3137, 3144, 3180, 3310, 3343, 3372 and 3396 cm^{-1} (Fig. 3).

In some of our samples, we can find a small number of absorptions that were already mentioned in some historical ‘asteriated’ hydrogen-rich diamond by Rondeau et al. [24]. Peaks at 3050 and 3154 cm^{-1} are sometimes encountered in chameleon diamonds. They were present in cuboid sectors of asteriated diamonds but absent in octahedral sectors. Those at 2813 and 3186 cm^{-1} were encountered in all our samples (Fig. 3).

Finally it is possible to see in the spectra of some chameleon diamonds numerous weak peaks which have not been, to the best of our knowledge, reported in the consulted literature. These are at 3163, 3206, 3214, 3259, 3271, 3282 (Fig. 3), 4545 and 6212 cm^{-1} (Fig. 1).

6.4. UV Visible NIR absorption

The general appearance of typical UV Visible absorption spectra of chameleon diamonds is in conformity with their greyish yellowish-green color. All spectra show a continuum of increasing absorption toward the ultraviolet, starting at about 600 nm with the transmission window between 500 and 600 nm, the yellowish green part of the visible spectrum. A very broad band centred at about 800 nm is also visible, extending from about 650 nm to the near-infrared. There are also a weak, broad band centred at approximately 480 nm and a weak, moderately broad band at 427 nm. All these features are more easily observed on spectra taken at liquid nitrogen temperature. In addition, a number of weak, sharp bands at 474, 546, and 563 nm are visible for some of the stones (Fig. 4). They have

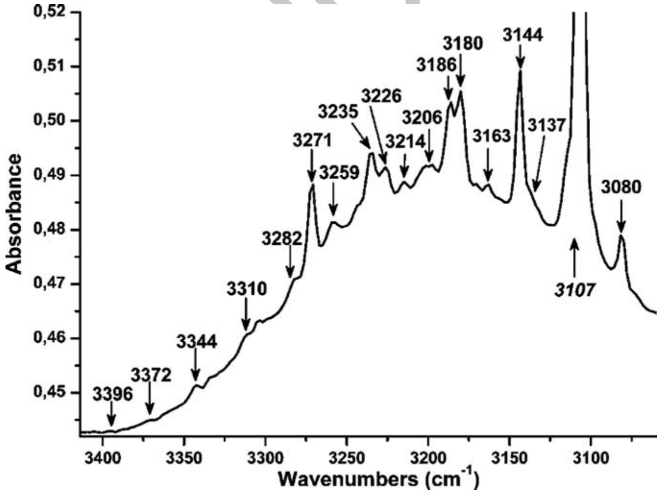

Fig. 3.

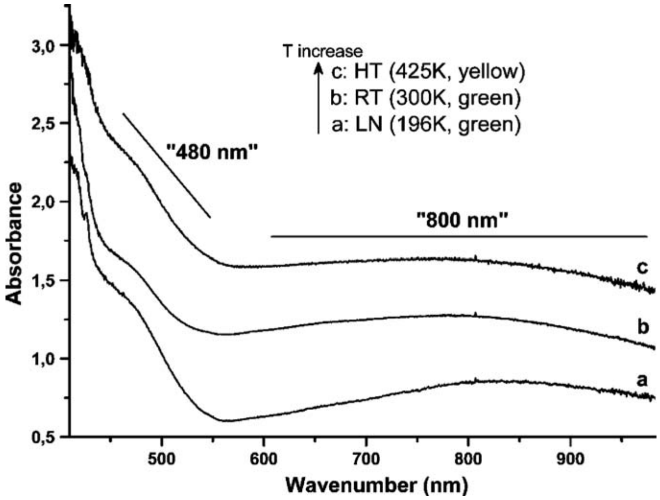

Fig. 5.

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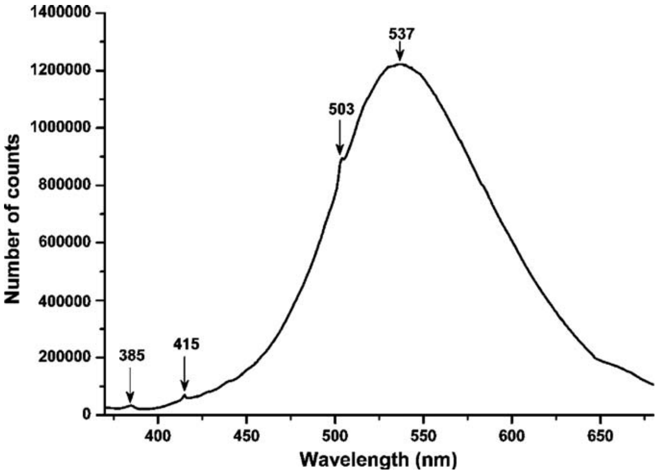

Fig. 6.

been formerly attributed to hydrogen-related centres in the “brown to greyish yellow family” of H-rich diamonds [6].

Other investigators observed very weak and sharp lines at about 792, 468 nm, and 648 nm, which are attributed to Ni-related centres [25,26]. The 767 nm absorption was observed in some nitrogen-containing synthetic diamonds that were grown in nickel and subsequently annealed to 1600–1900 °C [25]. The 583 nm absorption was observed in the spectrum of HPHT-treated diamonds [27]. Very weak and sharp unknown lines at about 523, 570, 664, 775 and 840 nm are also present (some are visible on Fig. 4).

Sometimes a moderate to strong absorption due to the N3 centre (415 nm) and the associated vibronic structure (405 and 396 nm) are superimposed to the previously defined features.

Three different UV Visible spectra of a typical sample with well observable color change were obtained at three different temperatures in order to show the origin of the thermochromic effect. At liquid nitrogen temperature (Fig. 5a) the very broad absorption around 800 nm is relatively strong (metastable green color) and as soon as the temperature increases (Fig. 5b and c) this band tends to decrease to become finally very weak when the diamond is heated (stable yellow color). The 480 nm band broadens and weakens somewhat with heat (Fig. 5).

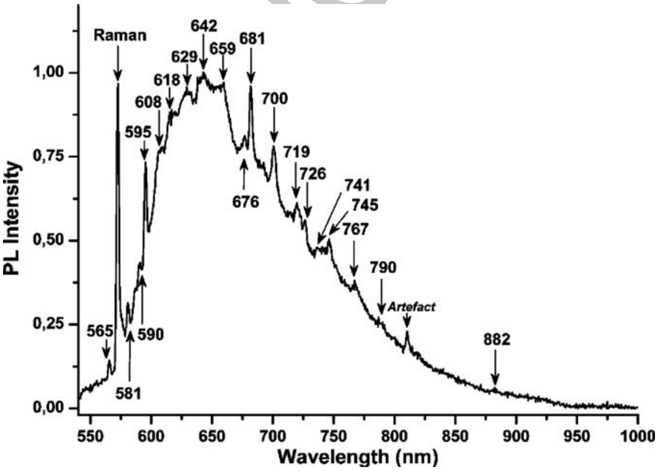

Fig. 7.

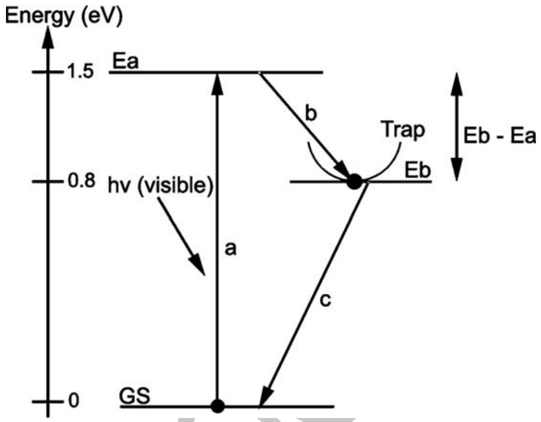

Fig. 8.

So in terms of UV Visible spectroscopy, the yellow state corresponds to the presence of a continuum with the 480 nm and 427 nm bands superimposed, whereas in the green state, the very broad band centred at about 800 nm is added to these features. Thus the progressive removal of the very broad band is responsible for the change of color. In other terms, it is the cause of the chameleon effect, and to the best of our knowledge this was never observed in diamonds without such an effect.

6.5. Photoluminescence behaviour

Chameleon diamonds all fluoresce very strongly under ultraviolet radiation with a weak to moderate chalky (i.e. turbid) luminescence. In long wave (LW) ultraviolet, they emit a strong to very strong yellow fluorescence. For the light stones the emission is whitish yellow (because of the combined presence of both blue – due to N3 – and yellow luminescence), and always strong. A few diamonds show an orange component to the luminescence color. The short-wave (SW) ultraviolet reaction is similar in color to that in long wave, but always lesser or equal in intensity.

In both ultraviolet radiations the strong luminescence is followed by a moderate to strong yellow phosphorescence that decays slowly over a period of a few minutes to half an hour.

The typical luminescence spectra of chameleon diamonds show, for a 365 nm excitation wavelength (Fig. 6), a strong broad band centred at about 537 nm (in the green range) and a comparatively very weak band at 503 nm (the H3 centre). The 537 nm band probably corresponds to the emission systematically associated with the 480 nm broad band seen in UV Visible absorption spectra [28]. Other features are possibly encountered in some chameleon diamonds, such the N3 centre (415 nm) and a weak broad band at 385 nm.

For the same chameleon diamond, but for an excitation wavelength of 532 nm, the photoluminescence spectrum is shifted, the main broad band is now centred at about 630 nm and there are many superimposed weaker bands (Fig. 7).

The broad band centred at about 630 nm is seen in type IaA/Ib orange to orangey-yellow diamonds that exhibit the 480 nm band [7].

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There are numerous peaks that are common to the luminescence spectra of all chameleon diamonds recorded for an excitation wavelength at 532.7 nm. Most of them were encountered on the spectrum of a Ni-rich high pressure – high temperature – treated synthetic diamonds (575, 581, 590, 608, 618, 642, 650, 659, 681, 700, 719, 726, 745, 790 and 882 nm) [7]. All chameleon diamonds studied present a weak emission at 741 nm (GR1 centre).

7. Discussion

Even if all parameters are not yet well understood chameleon diamonds present numerous typical characteristics that could be encountered separately among other fancy colored diamonds but must be present together. Chameleon diamonds could arguably be described as a mixture of a yellow to orange diamond showing a 480 nm band (possibly with a type Ib character) with a greyish-green H-rich diamond. The presence of cuboid growth sectors implies moreover a particular growth history.

Chameleon diamonds are type Ia and commonly hydrogen-rich, which implies a relatively high nitrogen content, as observed. UV Visible spectra confirm the presence of hydrogen-related defects. On the basis of spectroscopic data, the diamonds would be classified as the “brown to greyish yellow family”, a sub-class of H-rich diamonds [6]. This character is typically associated with cuboid growth. In the range of 3000–3400 cm^{-1}, the presence of numerous infrared bands related to a type Ib character [9] and the 480 nm band (with its companion line at 427 nm) implies indirectly the presence of isolated nitrogen [8]. However the continuum rising fairly steeply from about 560 nm toward the UV is typical of that in yellow pure type Ib synthetic diamonds. The fact that one of the bands deemed characteristic of isolated nitrogen is very weak (1130 cm^{-1}) and the other absent (1344 cm^{-1}) at the resolution used is still unexplained. The presence of nickel or nickel-related centres in chameleon diamonds as indicated by some typical UV Visible centres was furthermore confirmed by EDXRF chemical analysis. In three samples for which we had the time and opportunity to perform EDXRF analysis, a distinct Ni signal was obtained for a 1000 s measurement time (deadtime 30%). It is now felt that some Ni is typically associated with cuboid H-rich sectors [29]. Thus three factors could be involved in the thermochromic and photochromic process of chameleon diamond: a hydrogen-related centre, a weak uncommon type Ib character with an associated 480 nm band, and the presence of Ni or Ni-related centres. Neither of these factors, taken separately, leads to a chameleon behaviour.

As Ni-related defects are often associated with hydrogen, we could more simply define chameleon diamonds as H-rich diamonds with a 480 nm band. We propose to limit the use of the term “chameleon diamond” to describe those diamonds whose light-absorbing properties are altered upon both optical and thermal excitations, named respectively photochromic and thermochromic effect. The change of color must be between an essentially yellow color to an essentially greyish-green to green color. Other behaviours cannot be described as chameleon; a different nomenclature must be used.

It should be noted that some of our observations disagree with those by De Weerdt and Van Royen [10]. We do not see a change of color when the diamonds are cooled from room temperature to liquid nitrogen temperature. Neither do we see a change of color after UV illumination. However, our observations are consistent with those of Hainschwang [7] and others in the gemmological laboratory community (Franck Notari, pers. comm. 2006).

Finally, we now propose a tentative model to explain all properties described above. This model is based on an electronic approach and on an atomic approach trying to explain both the thermochromic and photochromic behaviour responsible for the chameleon effect.

It is known that coloration processes imply electronic transitions between at least two different energy levels. For chameleon diamonds, the yellow to green change requires thus at least one electronic transition. This transition is reversible because the change is reversible. Yellow is the color observed after a period in the dark. So, before being submitted to visible light the color centre is in its lowest energy state, so that, yellow should be seen as the stable color for chameleon diamonds. The green color is then the metastable color. As soon as the diamond is exposed to light, the color remains green, implying a specific electron trap in the system. The shorter the life time of states implied in an electronic transition, the broader the corresponding absorptions. The broad band centred at about 800 nm in chameleon spectra is therefore possibly related to a short life time centre. The fact that this band is large implies a non-vibrational phenomenon, confirmed by the observation of the transition at low temperatures.

We propose the following energy diagram with three states, a fundamental one (GS), an excited one with a short lifetime (Ea) and an metastable one (Eb) (Fig. 8).

When the defect is in its stable state, i.e. when no external energy is received (for instance when the diamond is in a safe), this diamond is yellow. Once exposed to visible light, it is exposed to electromagnetic radiations. Some of this radiation will be absorbed and some electrons will be promoted to the excited state (Fig. 8, a), then about 1.55 eV is absorbed (i.e. about 800 nm) in this electronic transition. This electron may fall in a potential well and be trapped on the Eb level (Fig. 8, b). In this metastable state, the diamond appears green. The change from the yellow stable color to the green metastable color takes a few seconds because populating the Eb level is not instantaneous. As long as the diamond is submitted to visible light it stays in its green state. If the depth of the trap ΔE (=Eb−Ea, Fig. 8) is wide compared to k_BT (the thermal activation energy), then the probability for the electrons to jump outside the trap at room temperature is negligible and then electrons remain in the metastable level. The chameleon diamond stays green.

Thermochromic behaviour:

If the diamond is placed at a moderate temperature of 150 to 200 °C, k_BT becomes non-negligible compared to the potential barrier. The electron can then escape the trap and return to the fundamental state GS (Fig. 8, c). The chameleon diamond will turn yellow and the broad band in the UV Visible absorption spectra will disappeared. This is what is observed. Observation

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shows that chameleon diamonds are green at liquid nitrogen temperature. This is in agreement with the model described above. At low temperature, k_BT is very small and electrons remain in the trap: the diamond is green.

Photochromic behaviour:

If the diamond is placed in the dark, then there is no visible radiation. No electrons are promoted to the Ea then Eb level. Those already in the Eb level go back slowly to the fundamental state. This process is then slower than when the diamond is heated, this in conformity with observations.

Photoluminescence behaviour:

The triplet state also explains the lasting phosphorescence of the stones. It has been estimated that long lasting phosphorescence corresponds to a trap depth of approximately 0.7 eV [30]. The emission being at about 2.31 eV, the de-excitation is made toward an electronic level lower in energy than the starting one.

Thus the proposed energy diagram (Fig. 8) explains all observed properties. A possible atomic model may be inferred from existing literature. The most plausible model describing the 3107 cm^{-1} hydrogen-related centre in diamond is N ... H–C [31]. Photochromic materials in which hydrogen plays a role in the color changing mechanism are known [32], and they first attracted our attention to a possible H-related photochromic defect. However, since these materials are essentially ionic crystals (polyoxomolybdates), and diamond is covalent, the mechanism cannot possibly be the same.

The centre responsible for the chameleon effect is only observed in diamonds with a strong IR absorption from A aggregates, a neighbouring substitutional nitrogen pair. It therefore seems reasonable to suggest that there may be a structural link between the A centre and our H-related centre responsible for the chameleon effect. The yellow stable state could correspond to a ground state configuration of a nitrogen–hydrogen complex. When absorbing a photon of about 1.55 eV (the broad band at 800 nm) the defect changes structure and the diamond turns green. Electrons are trapped at an intermediate level in the gap. As long as the system is exposed to light, it stays in this state, the diamond being green. If temperature increases or if the diamond is put in the dark, in other words, if there is respectively too much or not enough energy to keep electrons in the trap, the system returns to its stable state and the diamond turns yellow.

Such a nitrogen–hydrogen centre could be consistent with many infrared spectroscopic features observed in the spectra of chameleon diamonds. Infrared peaks related to the C–H bond are present (main peaks at 1405 and 3107 cm^{-1}) as well as one identified N–H-related peak at 3235 cm^{-1}. It is possible to observe unusual peaks related to isolated nitrogen, part of them already described [9]: 1238, 3137, 3144, 3180, 3310, 3343, 3372 et 3394 cm^{-1}, as well as a weak but distinct 1130 cm^{-1}.

This model also helps explain why chameleon diamonds are a rare combination. The type Ib character with the associated 480 nm broad band is necessary for the intense and saturated yellow to orange seen in the stable state. In a sense isolated nitrogen provides the “background” color. The high hydrogen content is necessary to provide the hydrogen of the nitrogen–hydrogen complex probably linked to the color change. This color change is not observed in all H-rich diamonds, as the electron trap is also necessary. As the trap is present only in chameleon diamonds, which have a type Ib character, it could be argued that the trap is provided by a level related to isolated nitrogen but we have no evidence for that. Alternatively, it is possible that the trap is related to a specific and probably rare Ni–H–N defect.

Further work is needed to establish the exact defects present and necessary to observe the chameleon effect. For example, it would be useful to explore the behaviour of H-related bands in the infrared with heating or illumination. However, with our current experimental setup and the limited time available for the study of each stone it was not possible to do so.

8. Conclusion

We propose a physical definition of chameleon diamond and a tentative model for the color change behaviour. Our work, as well as published literature demonstrates that chameleon behaviour necessitates the observation of both the photochromic and thermochromic behaviour (ex. given [7]). A chameleon diamond is a diamond which changes color from essentially desaturated green to an essentially yellow when kept in the dark (photochromism) and when gently heated (thermochromism). The model we propose demonstrates that these behaviours are interrelated and that one cannot exist without the other.

Chameleon diamonds are type IaA/B with [A]≫[B] and with moderate to high amounts of nitrogen, but only traces of type Ib, often indirectly detected. The presence of the weak, broad band centred at approximately 480 nm (with a companion line at 427 nm) is related to this weak type Ib character. Also chameleon diamond must contain some hydrogen (sometimes in unusually high concentrations). Some nickel-related centres are often observed as well, possibly because they are common in cuboid H-rich growth sectors. Chameleon diamonds all present a medium to strong yellowish to yellow fluorescence as well as a long lasting phosphorescence. All their UV Visible spectra present a very broad band centred at about 800 nm which diminishes to produce the yellow color. N3 and various hydrogen-related absorptions could be observed as well in the visible and near-infrared but they are not necessary for the chameleon behaviour.

We propose a model which explains all the spectroscopic properties and observed color behaviour of chameleon diamonds. It consists of an electron trap in the diamond band gap. We suggest the chameleon effect could be explained by an interaction between hydrogen and A aggregates, for example with photochromic and thermochromic behaviour of chameleon diamonds due to a switch between a ground and metastable excited state configuration.

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